Atomic cesium 3*d* core photoelectron spectrum

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The $3d_{3/2}$ photoelectron peak from atomic cesium and the shake-up satellites up to ~30-eV-higher binding energy have been studied with Al $K\alpha$ x rays (1487 eV). At ~22 eV from the $3d_{3/2}$ peak satellites corresponding to excitation from the 5*p* levels have been observed with an intensity 5% that of $3d_{3/2}$. Accordingly, the shoulder observed previously by Mathews *et al.* on the high-binding-energy side of the $6s \rightarrow 7s$ shake-up associated with $3d_{3/2}$ ionization has now been assigned to shake-up from the 5*p* levels accompanying $3d_{5/2}$ ionization. This conclusion has necessitated a lowering of the estimated $6s \rightarrow 7s$ relative intensity from ~18% to ~14%. Comparison with sudden-approximation intensity calculation shows that they overestimate the relative intensities for $ns \rightarrow (n+1)s$ shake-up in Na, K, and Cs. These intensities decrease in going down the group, as shown by both theory and experiment.

Banna *et al.*[1] were the first to observe the presence of shake-up photoelectron peaks in the 3*d* core region of atomic cesium. By analogy with the assignment of similar satellite structure in the 1*s* core spectrum of sodium,[2] it was clear that the strongest feature was due to $6s \rightarrow 7s$ excitation accompanying ionization from one of the spin-orbit-split 3*d* levels. More recently, Mathews *et al.*[3] took a closer look at the 3*d* region in an attempt to characterize the shake-up structure in more detail. They concentrated on the high-binding-energy side of the $3d_{3/2}$ spin-orbit component rather than the $3d_{5/2}$ because the Al $K\alpha_{1,2}$ exciting line (1487 eV) employed is known to have x-ray satellites ($K\alpha_{3,4}$) up to ~12-eV higher energy which, given that the $3d_{5/2}$ is at 14.0 eV (Ref. 1) lower binding energy than the $3d_{3/2}$, will overlap severely with the shake-up satellites of interest. This overlap can clearly be seen in the earlier spectrum of Banna *et al.*[1] Mathews *et al.*[3] concluded the following. At least two satellites are present on the high-binding energy side of the $3d_{3/2}$ peak, one 5.3(2) and the other 7.7(3) eV above $3d_{3/2}$. Their intensities relative to the main peak are 13.4(6)% and 4.2(5)%, respectively. These two satellites were tentatively assigned to $6s \rightarrow 7s$ and $6s \rightarrow 8s$ excitation accompanying core ionization.

Shake-up in the core ionization of atoms continues to receive considerable attention from theorists. For example, Dyall[4] studies the 1*s* ionization in argon and de Alti *et al.*[5] performed both relativistic and nonrelativistic Hartree-Fock calculations for the shake-up lines resulting from core ionization of the alkali-metal atoms. More recently, Selvaraj and Gopinathan[6] used the relativistic exchange RΞ method to carry out transition-state calculations of the shake-up energies for both the rare gases and the alkali-metal atoms. Both they and de Alti *et al.*[5] also calculated relative intensities of the shake-up peaks using the sudden approximation.[7] The two sets of calculations support the assignment[1,3] of the first shake-up peak to $6s \rightarrow 7s$ but agree that the intensity of the $6s \rightarrow 8s$ shake-up is very low, being around 0.4–0.5% of the main peak. Similar results were found for the other alkali-metal atoms; that is, the $ns \rightarrow (n+2)s$ transition is substantially weaker than the $ns \rightarrow (n+1)s$ transition.

Other explanations for the shoulder observed by Mathews *et al.*[3] were next sought by de Alti *et al.*, after the $6s \rightarrow 8s$ assignment was ruled out. They suggested the possibility of configuration interaction in the final state redistributing the total 7*s* intensity. Indeed, Aksela and Aksela[8] concluded that the 3*d* hole state of cesium is well described by the $3d^9(6s+5d)$ atomic state, due to the collapse of the 5*d* wave function to smaller radius in going from neutral to singly ionized cesium. de Alti *et al.*[5] discounted the possibility of mixing between 7*s* and 8*s* states, however, since they are Rydberg states and since mixing between singly excited configurations should be small by Brillouin's theorem. Thus work to data has not yielded a definitive assignment for the second shake-up structure. Rather, some doubt has been cast about the validity of the experimental results.

Here we report a more complete shake-up spectrum and show that a hitherto overlooked transition (in this system) is most likely responsible for the bulk of the structure observed on the high-binding-energy side of the main shake-up structure. Our results, therefore, further confirm that the previously observed features[1,3] are real. To be sure it was clear to us from the outset that an experimental artifact was unlikely since the same results were obtained using two different spectrometers[1,3] (admittedly having one operator in common) and the possibility of electron-energy-loss peaks was ruled out since the $6s \rightarrow 6p$ transition in neutral cesium would be found only ~1.4 eV from the main peak.[9] We argue below that the excitation responsible for the second satellite is $5p \rightarrow 6p$ accompanying $3d_{5/2}$, rather than $3d_{3/2}$, ionization.

The excitations $np \rightarrow (n+1)p$, where *n* is for the outermost occupied shell are the ones primarily responsible for shake-up in the rare gases. In xenon, for example, Gelius[10] found the $5p \rightarrow 6p$ transition to have an intensity 6.4% that of the main 3*d* peak and the $5p \rightarrow 7p$

transitions ~2.9% of the main peak. It is likely that the analogous transitions in the next element cesium will be somewhat less intense, since Carlson *et al.*[11] calculated the probability for shake-off (as a result of β decay) of the $5p$ electrons to decrease from ~12% in xenon to ~7% in barium. Nevertheless, $5p$ shake-up should occur with observable intensity in cesium.

In order to prove our thesis we have remeasured the cesium shake-up spectrum and have carried out semiempirical calculations to predict the position of the $5p \rightarrow 6p$ shake-up peaks. It is possible to calculate the separation between the $3d_{5/2}$ peak and the shake-up peak in question using the results of previous work. Combining the separation of the shake-up peak[3] from the $3d_{3/2}$ peak of 7.7 eV with the $3d$ spin-orbit splitting of 14.0 eV (Ref. 1) we get a value of 21.7 eV. If our assignment is correct then there should be peaks at this separation from the $3d_{3/2}$ peak on the high-binding-energy side. In Fig. 1 a spectrum of the $3d_{3/2}$ core region is displayed which extends to higher binding energy than any previously reported spectra, covering a region more than 30 eV above the $3d_{3/2}$ peak. It was obtained using a spectrometer constructed specifically for high-temperature gas-phase work.[12] As expected, a broad peak is observed centered at 21.6 eV from the main peak. This is strong evidence that the previously unassigned peak labeled B in Fig. 1 is part of the $3d_{5/2}$ manifold.

Additional evidence can be obtained from calculations. Desclaux's relativistic Hartree-Fock program[13] is known to give accurate binding energies from ΔSCF (self-consistent field) calculations, in which the total energies of the neutral and core-ionized atom are calculated. Unfortunately, this program cannot calculate energies of atoms with two open shells of the same symmetry. We have therefore obtained approximate shake-up energies by calculating the energies of the $5p_{1/2} \rightarrow 6p_{3/2}$ and the $5p_{3/2} \rightarrow 6p_{1/2}$ transitions in $3d_{3/2}$ core-ionized cesium. We obtained 22.0 and 19.9 eV, respectively, in good agreement with the observed ~22-eV separation. The $5p_{1/2}$-$5p_{3/2}$ spin-orbit splitting is known experimentally[14] to be about 1.8 eV (this value is also obtained from the orbital energies of neutral cesium calculated using Desclaux's program). Combining this with the calculated transition energies above gives 20.2 eV for $5p_{3/2} \rightarrow 6p_{3/2}$ and 21.7 eV for $5p_{1/2} \rightarrow 6p_{1/2}$. Similar calculations give 24.2 and 25.7 eV for $5p_{3/2} \rightarrow 7p_{3/2}$ and $5p_{1/2} \rightarrow 7p_{1/2}$, respectively. We conclude, therefore, despite the approximate nature of these values that these transitions are indeed responsible for at least a good part of the structure labeled B in the figure.

Obtaining a reliable relative intensity is difficult due to the large number of multiplet terms arising from the configuration with open $3d$, $5p$, $6p$, and $6s$ shells and the insufficient resolution. Mathews *et al.*[3] obtained 4.2% for peak B relative to $3d_{3/2}$. From the spin-orbit intensity ratio of 1.48 (Ref. 15), peak B is ~3% of $3d_{5/2}$. In view of the present findings, their values should probably be revised since they assumed equal linewidths for the main peak as for the two shake-up peaks. Their assumption was reasonable since peak B was then assigned to

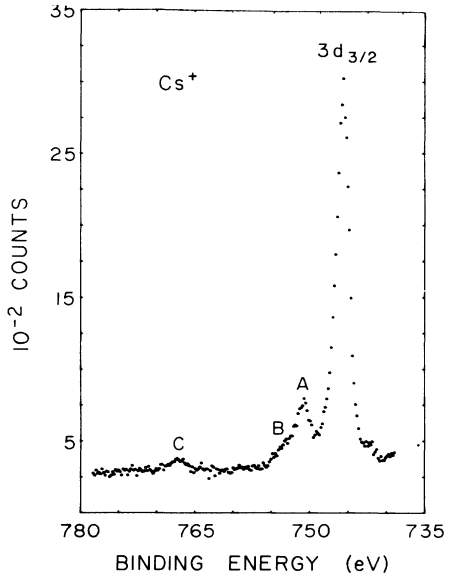

FIG. 1. The $3d_{3/2}$ region of atomic cesium. The peak labeled B corresponds to shake-up involving excitation of $5p$ electrons accompanying $3d_{5/2}$ ionization. (The latter peak is at 14.0 eV lower binding energy from $3d_{3/2}$ and is not shown.) Peak C is due to similar excitations accompanying $3d_{3/2}$ ionization while peak A is due to $6s \rightarrow 7s$ excitation. A fit of four Lorentzians to the data gives linewidths of 1.8 eV for $3d_{3/2}$ and peak A (constrained to be equal) and 3.3 eV for peaks B and C (also constrained to be equal).

$6s \rightarrow 8s$ transitions. It is now clear, however, that peak B is broader than originally thought. We have therefore performed a nonlinear least-squares fit of Lorentzians to the experimental data points, constraining peaks B and C to have equal linewidths and peak A and $3d_{3/2}$ to have equal linewidths as well. Our fit yielded a separation of 5.1(1) eV, which is within the error limits of the separation reported by Mathews *et al.*[3] For peaks B and C we obtained separations of 7.0(4) and 21.6(3) eV, respectively, with the peak-B separation also falling within the error of the previously measured value.[3] For the relative intensities, however, we measured 13.6(14)%, 8.9(25)%, and 5.7(12)%. Here only the relative intensity of peak A is in good agreement with past measurements.[3] We attributed the higher value obtained here (Mathews *et al.* obtained 4.2%) for peak B to the assumption of a greater full width at half maximum than done previously. This, however, is reasonable as argued above. Note that the ratio of structure B to C is 1.6:1, close to the expected $3d_{5/2}$:$3d_{3/2}$ intensity ratio. Thus, despite the difficulty of fitting overlapping peaks, our approach yields consistent results.

We are now in a position to better compare theory and experiment in the case of the main shake-up transition, $ns \rightarrow (n+1)s$. Table I lists relative intensities for three of the alkali-metal atoms, Na, K, and Cs. It is seen that the calculations[5,6] overestimate the shake-up intensity in every case,[16] with the relativistic local-density RΞ-method calculations[6] agreeing somewhat better with experiment than the Hartree-Fock results.[5]

TABLE I. Relative intensities of the $ns \rightarrow (n+1)s$ shake-up in some alkali-metal atoms (percent of the main line).

Atom (Level)	Expt.	Intensity Nonrelativistic[a]	Relativistic[b]
Na($1s$)	19[c]	23	24
K($2p$)	18[d]	21	20
Cs($3d$)	14[e]	19	17

[a]Hartree-Fock calculations from Ref. 5.
[b]Relativistic local-density RΞ method calculations from Ref. 6.
[c]From Ref. 2.
[d]From Ref. 16.
[e]This work.

An interesting trend emerges. In going from sodium and potassium to cesium, the $ns \rightarrow (n+1)s$ intensity *decreases*. This can be seen from theory,[5,6] but is only now seen to be definitely supported by the experimental results.

Higher-resolution spectra are needed for a complete characterization of the entire Cs shake-up manifold. Furthermore, the $3d_{5/2}$ region should be included in a more complete study. Unmonochromatized Al $K\alpha$ x rays are far from ideal in this case in part because of their width and in part because of the fortuitous overlap of the $3d_{5/2}$ shake-up with the $K\alpha_{3,4}$ x-ray satellites.[1] We know of no effort underway to study high-temperature species with monochromatized laboratory sources. However, synchrotron radiation would be very well suited for these studies and we plan to use it in the near future. A study of the $np \rightarrow (n+1)p$ transitions in other alkali-metal atoms, especially Na and K would also be of interest and is underway.

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